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Structure, spectroscopy, and thermal decomposition of 5-chloro-1,2,3,4-thiatriazole: a HeI photoelectron, infrared, and quantum-chemical study

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ABSTRACT

5-Chloro-1,2,3,4-thiatriazole has been investigated in the gas phase for the first time by mid-infrared and He I photoelectron spectroscopy. The ground-state geometry has been obtained from quantum-chemical calculations at the CCSD(T) and B3LYP levels using aug-cc-pVTZ basis set. Ionization potentials have been determined and the electronic structure has been discussed within the frame of molecular orbital theory. IR and photoelectron spectroscopies, supported by quantum-chemical calculations at the B3LYP and SAC-CI levels, provide a detailed investigation into the vibrational and electronic character of the molecule. Thermal stability of 5-chloro-1,2,3,4-thiatriazole has been studied both experimentally and theoretically. Flash vacuum thermolysis of the molecule produces fast quantitatively N₂, ClCN, and sulfur. Theoretical calculations at the CCSD(T)//B3LYP level predict competitive decomposition routes, starting either with a retro-cycloaddition reaction leading to N₂S and ClCN or with a ring opening to chlorothi carbonyl azide intermediate, to produce finally N₂, S, and ClCN. Calculations also predict that N₂S is reactive and decomposes in bimolecular reactions to N₂ and S₂.

Keywords

structure, thermolysis, IR, UPS, ab initio, DFT

The paper is dedicated to Magdolna Hargittai on the occasion of her 70th birthday.

Introduction

1,2,3,4-Thiatriazoles are well-known heterocyclic compounds, with a history going back to the XIXth century [1–3]. A wide range of organic derivatives have been prepared following the 1950s [3–7]. Thiatriazoles are known to be thermally unstable and decompose upon mild heating or even at room temperature to sulfur, nitrogen, and nitriles. Their thermal stability, however, strongly depends on the substituent attached to the ring carbon atom. Aryl and substituted amino- and thio-derivatives are relatively stable and have found applications due to their interesting biological properties, including fungicidal, antitubercular, antiviral, anticancer, and muscle stimulant activity [7]. Alkyl, aralkyl, and alkoxy derivatives are unstable, isolated only at low temperature, and often present explosion danger at ordinary conditions [3–7]. The only known halogen derivative, the 5-chloro-1,2,3,4-thiatriazole is highly explosive [8]. It has been used in nucleophilic reactions for the synthesis of substituted amino- and alkoxy-thiatriazoles [6–8]. Very little is known experimentally about the structure of unstable thiatriazoles, and 5-chloro-1,2,3,4-thiatriazole has never been studied by any experimental or theoretical methods to date. Structure and properties of a few relatively stable aryl-, amino-, and thio-derivatives have been studied by X-ray crystallography, NMR, IR, UV, and Raman spectroscopy (see reviews [6,7] and references cited therein).

In this work, we present the gas-phase characterization of 5-chloro-1,2,3,4-thiatriazole molecule, the study of its decomposition in the gas phase, and an investigation of its electronic and geometric structure by quantum-chemical methods and gas-phase spectroscopy. The latter includes He I ultraviolet photoelectron spectroscopy (UPS) and mid-infrared (IR) spectroscopy.

Experimental procedure

5-chloro-1,2,3,4-thiatriazole was synthesized and evaporated for gas phase investigations by adapting a known literature procedure [8], as follows. Temperatures of all equipments (flasks and separating funnels) and solvents kept at 0 °C during the synthesis, and an inert nitrogen atmosphere was used. 2 g (30.8 mmol) of sodium azide was dissolved in 50 ml of water and the solution was cooled down to 0 °C. 3.54 g (30.8 mmol) of thiophosgene was added to the solution dropwise in 30 min, and the suspension was stirred for additional two hours. The reaction mixture was extracted two times with 25 ml of cold diethyl ether, and the combined organic phase was dried over anhydrous magnesium sulfate for at least an hour. Drying agent was filtered off on a pre-cooled funnel. The solution is transferred into a flask

and the ether solvent is removed in vacuum at 0 °C. The flask is then connected via a vacuum stopcock to a vacuum system (practically to spectrometers) and pumped for about three hours to remove all traces of side products, unreacted thiophosgene, and water, while keeping the temperature of the flask at 0 °C.

The thermolysis of gaseous 5-chloro-1,2,3,4-thiatriazole was carried out in a quartz tube (6 mm i.d.) heated along 30 cm using an electrical furnace. The effluent from the tube led directly into the IR cell or photoelectron spectrometer. The distance between furnace and detection point was 40 cm.

The IR spectrum (resolution 1.0 cm⁻¹) of gaseous 5-chloro-1,2,3,4-thiatriazole was recorded on a Bruker IFS 28 FT-IR spectrometer equipped with a 22 cm single-pass glass cell. The cell, with KBr windows, gave a spectral range from 4000 to 400 cm⁻¹. The effluent from the sample container was pumped continuously through the cell using a rotary vacuum pump while maintaining the temperature of the container at 0 °C and the pressure in the cell at 0.3 mbar.

The He I ultraviolet photoelectron spectrum (UPS) of the gaseous thiatriazole derivative and its pyrolysis products were recorded using an Atomki ESA-32 photoelectron spectrometer described in detail elsewhere [9]. Photoelectron spectra were recorded using the constant transmission energy mode of the electron energy analyzer and were calibrated with the Ar⁺(²P_{3/2,1/2}) spin-orbit doublet. The resolution of the analyzer was 30 meV (fwhm for the Ar ²P_{3/2} line).

Computational details

The geometry of the ground state neutral 5-chloro-1,2,3,4-thiatriazole molecule was calculated using the CCSD(T) and B3LYP methods. The stability of HF and B3LYP wave functions were checked, and both wave functions were found to be stable. The CCSD *T1* diagnostic, using the CCSD(T) geometry, was 0.019, and single point CASSCF(10,10) calculations indicated that apart from the main HF configuration (weight 89%) there was no other important configuration (weight for any other configuration was smaller than 3%). Harmonic and anharmonic vibrational wavenumbers were calculated at the B3LYP level, and infrared intensities were calculated using the harmonic force field. Vertical ionization energies (IEs) were calculated using the Symmetry Adapted Cluster/Configuration Interaction (SAC-CI) and the Outer Valence Green's Function (OVGF) methods using the geometry obtained at the CCSD(T) level. Lowest energy paths for decomposition of 5-chloro-1,2,3,4-thiatriazole were calculated at the CCSD(T)//B3LYP level. The minima and the connecting

lowest energy paths between minima were calculated at the B3LYP level using an intrinsic reaction coordinate (IRC) approach which was also manually checked by proceeding along the given reaction coordinate and simultaneously relaxing all other bond lengths and angles. Stability check was performed for all calculated structures. In order to obtain the total energies, single point energy calculations were done on top of B3LYP geometries at the CCSD(T) level. Gibbs free energies (G) were obtained by correcting the CCSD(T) total energy with zero-point vibrational energy (ZPE) and thermal corrections calculated at the B3LYP level. ΔG°_{0K} values, for example, represent energy difference between ZPE corrected total energies.

All calculations were done using the aug-cc-pVTZ basis set. Only valence electrons were correlated in CCSD(T) and SAC-CI calculations. All calculations were performed with the GAUSSIAN-09 quantum chemistry package [10]. References to original theoretical methods are listed in the program package manual [11]. For characterization of the normal vibrational modes of 5-chloro-1,2,3,4-thiatriazole, the total energy distribution (TED), which provides a measure of the internal coordinate contributions, was determined [12,13].

Results and discussion

Calculated equilibrium structure and stability

Calculated structural data of 5-chloro-1,2,3,4-thiatriazole is presented in Table 1 and the structure and numbering of atoms are shown in Figure 1. CCSD(T) and B3LYP results are in good agreement with each other, the largest difference in bond length and bond angles is 0.014 Å and 0.7°, respectively. According to calculations, the molecule is planar, with C_s symmetry, and has singlet electronic ground state. The singlet ground state is more stable than the lowest energy triplet excited state by 282 kJ mol⁻¹ (ΔG°_{0K}) at the B3LYP level. Bond orders of 5-chloro-1,2,3,4-thiatriazole ring have been calculated by comparing the calculated bond lengths of the thiatriazole with those of molecules having typical single/double CN, NN, CS, and NS bonds (H₃C–NH₂ (1.464 Å)/ H₂C=NH (1.264 Å), H₂N–NH₂ (1.433 Å)/*trans*-HN=NH (1.235 Å), H₃C–SH (1.830 Å)/ H₂C=S (1.611 Å) and H₂N–SH (1.733 Å)/HN=S (1.570 Å), calculated at the B3LYP level), using the Gordy's rule [14]. N₂–N₃ and N₄–C₅ bonds, nominally double bonds, are between a single and a double bonds (bond order 1.81 and 1.78, respectively), and S₁–N₂, N₃–N₄, and C₅–S₁ bonds, nominally single bonds, are shorter than a S–N, N–N or C–S single bond (bond order 1.11, 1.35, and 1.48, respectively).

This tendency to bond order equalization is in agreement with the expected aromaticity of thiatriazoles [6,7]. This corroborates with the calculated nucleus independent chemical shift values of NICS(0)= −11.1 and NICS(1)= −11.2 (B3LYP/aug-cc-pVTZ). Negative NICS values indicate aromaticity. The S₁–N₂ bond of the molecule is close to a single bond, the weakest of ring bonds concerning bond orders, this being the point of cleavage upon thermal ring opening to the corresponding chlorothi carbonyl azide.

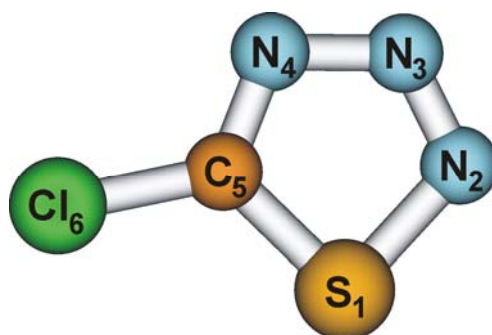


Fig. 1 Structure of 5-chloro-1,2,3,4-thiatriazole and numbering of atoms.

Table 1 Calculated^a equilibrium structure of 5-chloro-1,2,3,4-thiatriazole.

bond lengths / Å		bond angles /°	
S ₁ –N ₂	1.710 (1.713)	S ₁ C ₅ N ₄	113.3 (112.7)
N ₂ –N ₃	1.281 (1.267)	C ₅ N ₄ N ₃	110.2 (110.9)
N ₃ –N ₄	1.367 (1.353)	N ₂ N ₃ N ₄	116.8 (117.0)
N ₄ –C ₅	1.309 (1.301)	N ₃ N ₂ S ₁	110.9 (110.7)
S ₁ –C ₅	1.715 (1.715)	N ₂ S ₁ C ₅	88.9 (88.6)
C ₅ –Cl ₆	1.706 (1.707)	S ₁ C ₅ Cl ₆	123.8 (124.2)

^aCalculated at the CCSD(T) and B3LYP (in parenthesis) levels using the aug-cc-pVTZ basis set. See Figure 1 for numbering of atoms.

Thermal stability is a key issue for thiatriazoles, and the unimolecular stability is determined by the lowest energy path leading to bond dissociation or isomerization. Energetics of the lowest-energy decomposition paths for 5-chloro-1,2,3,4-thiatriazole are summarized in Table 2 and shown in Figure 2. Considering the initiating step, decomposition starts either with a retro-cycloaddition reaction leading to N₂S and ClCN via transition state **2** or by a ring opening to chlorothi carbonyl azide via TS **5**. N₂S decomposes in a second step to singlet sulfur atom, S(¹D), and nitrogen molecule (**1**→**2**→**3**→**4**, see Figure 2). The formation of ground state triplet sulfur, S(³P), in this process is spin forbidden.

Chlorothiocarbonyl azide, **6**, can isomerize with rotation around the C–N bond to azide **8**, and both azide decompose with N₂ loss to chloroisocyanate (**1**→**5**→**6**→**13**→**14**) and chlorothiazirine (**1**→**5**→**6**→**7**→**8**→**9**→**10**), respectively. These latter molecules either decompose in a consecutive step via ClCNS or directly to N₂, ¹S, and ClCN or isomerize to ClSCN. ClSCN, the thermodynamically most stable pseudohalide isomer, is possibly the best candidate for identification among the decomposition products of 5-chloro-1,2,3,4-thiatriazole. The overall barrier at the rate determining step for the retro-cycloaddition and azide routes is very similar, 110, 112, and 104 kJ mol^{−1} ($\Delta G^\circ_{298\text{K}}$) at TSs **2**, **13**, and **9**, respectively, thus these decomposition routes are competitive. Barriers are relatively low and explain thermal instability for 5-chloro-1,2,3,4-thiatriazole at room and elevated temperatures.

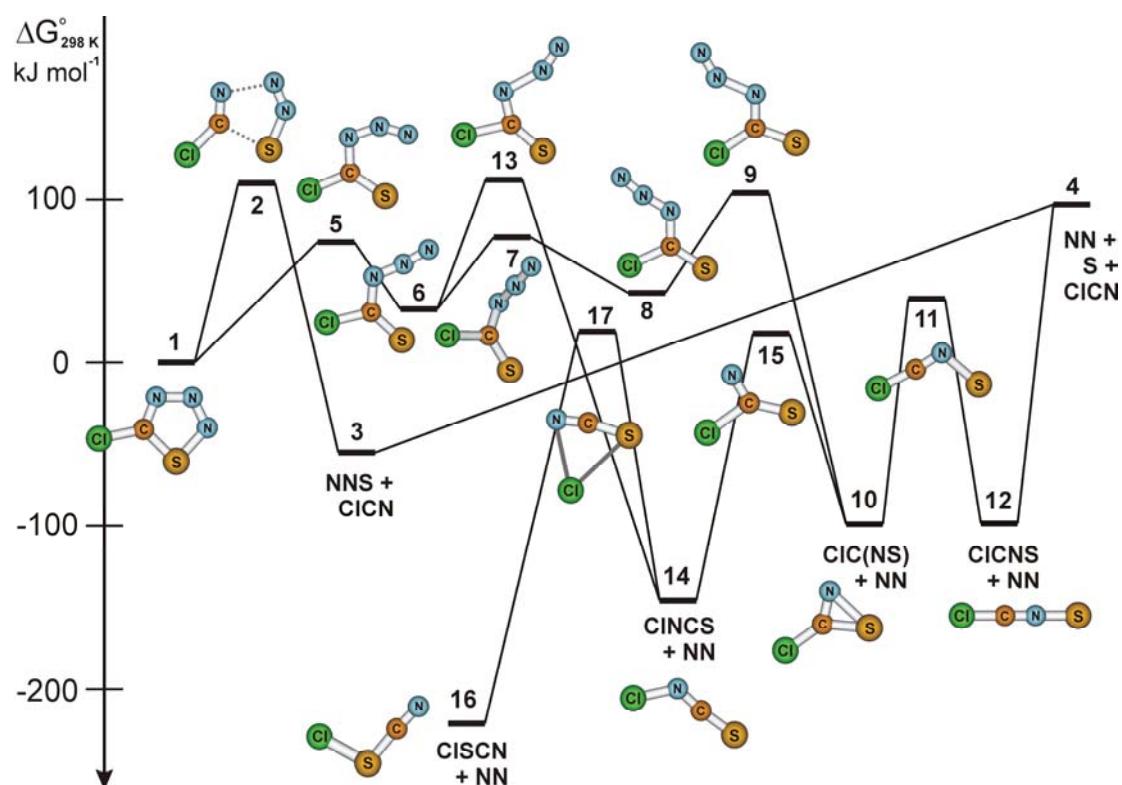


Fig. 2 Decomposition of 5-chloro-1,2,3,4-thiatriazole to ClCN, N₂, and ¹S. Gibbs free energies are relative to that of the 5-chloro-1,2,3,4-thiatriazole. Calculated at the CCSD(T)//B3LYP/aug-cc-pVTZ level.

Table 2. Energetics^a of the decomposition of 5-chloro-1,2,3,4-thiatriazole

Number	Description	ΔG_{298K}^o (ΔG_{0K}^o)
1	ClCN ₃ S	0 (0)
2	TS (1 \leftrightarrow 3)	110 (113)
3	NNS + ClCN	-55 (-14)
4	NN + S + ClCN	97 (167)
5	TS (1 \leftrightarrow 6)	74 (75)
6	ClC(S)N ₃	33 (36)
7	TS (6 \leftrightarrow 8)	77 (78)
8	ClC(S)N ₃	43 (47)
9	TS (8 \leftrightarrow 10)	104 (110)
10	ClC(NS) + NN	-99 (-55)
11	TS (10 \leftrightarrow 12)	40 (85)
12	ClCNS + NN	-98 (-56)
13	TS (6 \leftrightarrow 14)	112 (118)
14	CINCS + NN	-146 (-101)
15	TS (14 \leftrightarrow 10)	18 (62)
16	CISCN + NN	-221 (-175)
17	TS (14 \leftrightarrow 16)	19 (64)

^a Calculated at the CCSD(T)//B3LYP/aug-cc-pVTZ level. Energies (in kJ mol⁻¹) are relative to that of the 5-chloro-1,2,3,4-thiatriazole. See Figure 2.

N₂S is expected to be one of the key intermediates in the decomposition of thiatriazoles, and it is a crucial question if we can identify this molecule among pyrolysis products of 5-chloro-1,2,3,4-thiatriazole in this work (see below). N₂S has been identified among gas-phase thermolysis products of 5-phenyl-1,2,3,4-thiatriazole previously [15,16]. However, its identification in the gas phase is based on a special experimental setup, namely on a very short distance between furnace and detection point, allowing limited time for bimolecular reactions. N₂S, an *N*-sulfide, is very reactive and has been shown to decompose in bimolecular reactions in the gas phase to N₂ and S₂ [15]. To obtain information about the bimolecular reaction of N₂S, calculations have been performed at the CCSD(T)//B3LYP level (see Figure 3 and Table 3). In principle, bimolecular reactions between all possible species should be taken into account, however, *N*-sulfides and thiazirine are expected to be the most reactive and the only short-lived species in our experiment [16,17]. Therefore, we focus on these reactions. The lowest energy bimolecular decomposition path for two N₂S molecules is found to proceed via S–S bond formation, where two molecules of N₂S produce two molecules of nitrogen and singlet S₂ directly in a “tail to tail” (NNS...SNN) reaction after passing over a kinetic energy barrier of $\Delta G_{298K}^o = 76$ kJ mol⁻¹ ($\Delta G_{0K}^o = 46$ kJ mol⁻¹). There is no intermediate in this reaction, and the two N–S bonds simultaneously break, releasing nitrogen and S₂. The kinetic energy barrier of this reaction is relatively small, which clearly

explains the reactivity and instability of N_2S at room temperature if molecules interact with each other. Chloronitrile sulfide and chlorothiazirine, ClCNS and ClC(NS) , are also expected to be reactive and to take part in sulfur atom transfer reactions similarly to N_2S [16,17], thus bimolecular reactions between these molecules and N_2S have also been calculated (Figure 3). For comparison, the “tail to tail” reaction between two ClCNS molecules has also been computed. We note that this latter reaction was investigated by us earlier at the B3LYP/6-31G** level [18] and results are in agreement with the present work. Calculations predict similar decomposition mechanism for all of these investigated bimolecular reactions, with the formation of S_2 , nitrogen and/or ClCN . The kinetic energy barrier for all of these processes is small, between 53 and 68 kJ mol^{-1} ($\Delta G^\circ_{298\text{K}}$). Calculations thus predict that experimental observation of these species at room or higher temperatures requires the prevention of bimolecular reactions; *e.g.* working pressures and contact time should be kept low.

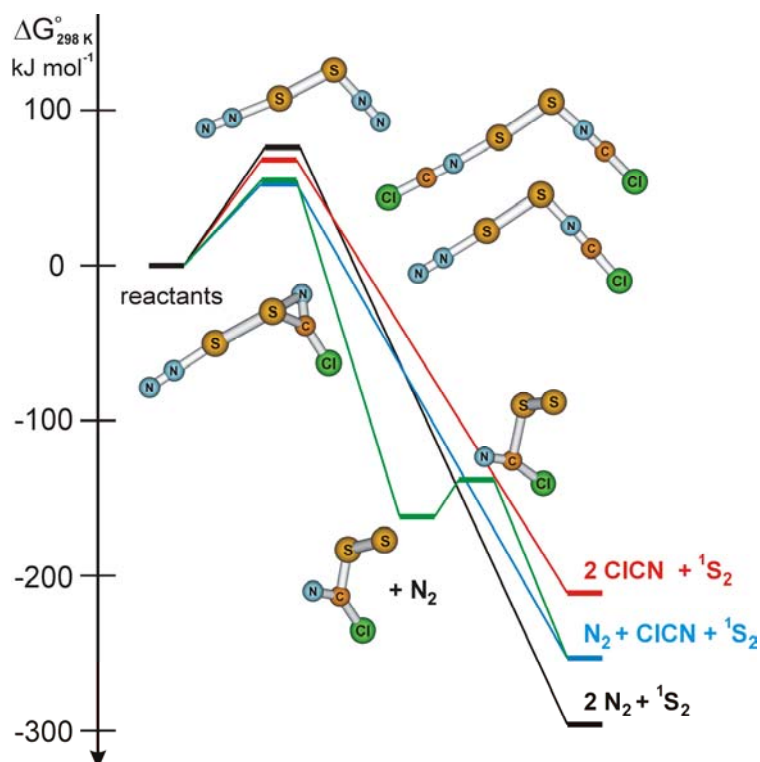


Fig. 3 Bimolecular decomposition of N_2S , ClCNS , and ClC(NS) , and the structure of transition states. Gibbs free energies are relative to that of reacting species. Calculated at the CCSD(T)/B3LYP/aug-cc-pVTZ level.

Table 3. Energetics^a of the bimolecular decomposition of N₂S, ClCNS, and ClC(NS)

Reactants	TS: ΔG_{298K}° (ΔG_{0K}°)	Products	P: ΔG_{298K}° (ΔG_{0K}°)
N ₂ S + N ₂ S	76 (46)	2 N ₂ + ¹ S ₂	-296 (-261)
N ₂ S + ClCNS	53 (21)	N ₂ + ClCN + ¹ S ₂	-253 (-218)
N ₂ S + ClC(NS) ^b	55 (19)	N ₂ + ClCN + ¹ S ₂	-252 (-220)
ClCNS + ClCNS	68 (36)	2 ClCN + ¹ S ₂	-211 (-176)

^a Calculated at the CCSD(T)//B3LYP/aug-cc-pVTZ level. Energies (in kJ mol⁻¹) are relative to that of the reacting species. Notation: TS= transition state, P= products. See Figure 3.

^b An intermediate is located on the singlet potential energy surface with a small barrier of $\Delta G_{298K}^{\circ} = 24$ kJ mol⁻¹ ($\Delta G_{0K}^{\circ} = 26$ kJ mol⁻¹) to decomposition to ClCN and ¹S₂.

Gas-phase IR spectrum

The IR spectrum of gaseous 5-chloro-1,2,3,4-thiatriazole is shown in Figure 4, with the experimental and calculated vibrational wavenumbers (including calculated IR intensities and the TED) listed in Table 4. The molecule has nonlinear planar structure, thus it has twelve normal modes of vibration, nine of which are in the molecular plane (a') and three are out-of-plane (a''). All vibrational modes are infrared active. The calculated wavenumbers and IR intensities are in good agreement with experiment and support the band assignments. The calculated values indicate that ten of the fundamentals should give rise to IR bands above the 400 cm⁻¹ cutoff of the instrument used in this experiment, however, one of them (ν_8) is not observed due to low IR intensity.

The asymmetry parameter κ of 5-chloro-1,2,3,4-thiatriazole, calculated using the computed B3LYP rotational constants, is -0.78, thus the molecule is a prolate asymmetric rotor ($\rho^* = 2.28$ and $\beta = 2.03$). The experimental fundamentals of a' symmetry are of A-type, B-type, or A/B-hybrid type, while those of a'' symmetry modes are C-type bands with pronounced Q-branches. Based on molecular constants above and equations published previously [19], the calculated *PR* separations for pure A, B, and C-type bands are 13, 10, and 19 cm⁻¹, respectively. The *PQR* structure is clearly observed on almost all IR bands in the gas-phase IR spectrum of 5-chloro-1,2,3,4-thiatriazole. The experimental *PR* separations for all A, B, and A/B type bands are in the range of 10–12 cm⁻¹, in good agreement with the predicted separations. Although out-of-plane ring deformations, possessing C-type bands, have very small IR intensity (1 km mol⁻¹, see Table 4), they could be identified by their prominent Q branch at 642 and 543 cm⁻¹. Detailed assignment of the IR spectrum is given in

Table 4, and the simplified assignment below is based on the major internal coordinate contribution. Total energy distribution (TED) of the normal vibrational modes indicates that vibrations are strongly mixed.

5-Chloro-1,2,3,4-thiatriazole exhibits no fundamental IR bands above 1400 cm^{-1} , and the most characteristic fingerprint of the molecule comprises the two medium and the strong intensity bands at 1375 , 1226 , and 1107 cm^{-1} , corresponding to C=N and N=N ring stretches and one of the ring in-plane deformations, respectively. The second ring in-plane deformation (ν_4) has very small IR intensity, and may be assigned to the very weak band at 1043 cm^{-1} . According to calculations, weak bands at 897 , 707 , and 611 cm^{-1} can be assigned to the N-N, C-S, and S-N ring stretches, respectively. There are two weak IR bands in the spectrum at 1146 and 1008 cm^{-1} whose assignment is ambiguous. Based on calculations, they are assigned to combination bands (see Table 4).

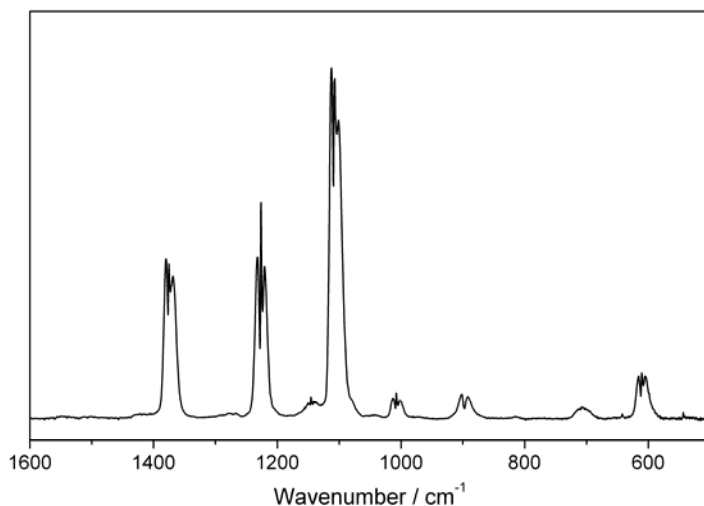


Fig. 4 Gas-phase IR spectrum of 5-chloro-1,2,3,4-thiatriazole

Table 4. Experimental and calculated vibrational wavenumbers (cm⁻¹) of 5-chloro-1,2,3,4-thiatriazole

Exp. ^a	Calc. ^{b,c}	Int. ^{b,d}	Assignment and description	TED ^e
1375 Q m	1367 (1400) a'	46	v ₁ C=N ring st	C ₅ N ₄ st(79), N ₂ N ₃ st(12)
1226 Q m	1251 (1304) a'	82	v ₂ N=N ring st	N ₂ N ₃ st(86)
1146 Q w	1166 (1184) a'		v ₅ +v ₉ ?	
1107 Q s	1076 (1099) a'	142	v ₃ ip ring def	r.b.(40), C ₅ Cl ₆ st(17), S ₁ C ₅ st(15)
1043 (?) vw	1003 (1037) a'	1	v ₄ ip ring def	r.b.(60), N ₃ N ₄ st(33)
1008 Q, w	982 (1022) a'		v ₇ +v ₈ ?	
897 w	900 (916) a'	11	v ₅ N-N ring st	N ₃ N ₄ st(58), r.b.(14)
707 w	681 (697) a'	4	v ₆ C-S ring st	S ₁ C ₅ st(55), r.b.(38)
642 Q (?) vw	641 (662) a''	1	v ₁₀ oop ring def	oop r.t.(93)
611 Q w	563 (586) a'	19	v ₇ S-N ring st	S ₁ N ₂ st(85), C ₅ Cl ₆ st(14)
543 Q (?) vw	551 (557) a''	1	v ₁₁ oop ring def	oop r.t.(93), C ₅ Cl ₆ wag(35)
n.o.	427 (436) a'	0.01	v ₈ Cl-C st	C ₅ Cl ₆ st(48), r.b.(20), S ₁ N ₂ st(10)
n.o.	266 (268) a'	2	v ₉ ip ClC bend	Cl ₆ C ₅ bend(84), S ₁ C ₅ st(11)
n.o.	237 (240) a''	1	v ₁₂ oop ClC wag	C ₅ Cl ₆ wag(58), oop r.t.(35)

^a Gas phase. Position of the most intense Q-band or the band centre is given. Abbreviations: s (strong), m (medium), w (weak), v (very). ^b Calculated at the B3LYP/aug-cc-pVTZ level. Isotopes: ¹²C, ¹⁴N, ³⁵Cl, ³²S. Asymmetric top parameters: $\kappa = -0.7823$, $\sigma = 17.3707$. ^c Anharmonic vibrational wavenumbers. Harmonic wavenumbers are in parenthesis. ^d In km mol⁻¹. Calculated using the harmonic force field. ^e Total vibrational energy distribution from force field analysis based on harmonic force constants. Contributions larger than 10% are provided. Abbreviations: st (stretching), r.b. (ring bend), r.t. (ring torsion), wag (wagging), oop (out-of-plane), ip (in-plane), def (deformation).

He I photoelectron spectrum

The He I photoelectron spectrum of 5-chloro-1,2,3,4-thiatriazole, together with calculated molecular orbital plots, is shown in Figure 5. Experimental and calculated ionization energies are listed in Table 5. We note that 5-phenyl-1,2,3,4-thiatriazole is the only thiatriazole derivative whose photoelectron spectrum was published to date [15], but assignment of the spectrum was not provided. The assignment of the photoelectron spectrum of 5-chloro-1,2,3,4-thiatriazole below is based on SAC-CI and OVGF calculations, and on the comparison with known spectra of relevant five-membered thiadiazoles [20,21].

The ground state electronic structure of 5-chloro-1,2,3,4-thiatriazole is ¹A₁. The sequence of molecular orbitals (MOs) deduced are ... (7a')²(1a'')²(8a')²(9a')²(2a'')²(10a')²(11a')²(12a')²(3a'')²(4a'')². A possible starting point to describe the electronic structure is to consider the MOs of a five-membered aromatic ring, modified with an exocyclic chlorine atom. Therefore, three π orbitals, three nitrogen 'lone pair' orbitals (n_N), and one sulfur 'lone pair' orbital (n_S) can be deduced from the thiatriazole

moiety as low IE MOs, as well as five high IE σ orbitals corresponding to five σ bonds of the ring. These MOs are augmented, and mix to some extent, with orbitals of the chlorine atom attached to the thiatriazole frame. Chlorine ‘lone pair’ orbitals (n_{Cl}) are expected to have low IEs. Photoelectron bands corresponding to high IE σ orbitals are not expected in the investigated IE region. MOs in general are delocalized over the entire molecular frame (see Figure 5), but in order to keep discussion simple and to provide the main character of the MO we use notations above.

Five bands are observed in the photoelectron spectrum of 5-chloro-1,2,3,4-thiatriazole (Figure 5), and according to calculations these bands originate from ionization of ten MOs (Table 5). The first photoelectron band has a complex structure, and calculations predict that it can be assigned to ionization from two ring π and two nitrogen ‘lone pair’ orbitals (n_{N}). The low IE side of the band shows vibrational fine structure with a weak adiabatic transition. The band shape thus indicates a geometrical change due to ionization and that a bonding electron is removed during ionization. The vibrational fine structure is not entirely resolved, but our best estimates indicate ionic vibrational wavenumbers of $810 \pm 50 \text{ cm}^{-1}$. This value, comparing to the wavenumbers of the neutral molecule (see above), may be assigned to the N–N ring stretch of the ground state radical cation. The assignment of the second band at 12.88 eV to one of the chlorine lone pair MOs is unambiguous considering the relatively narrow band shape and comparing the spectrum to those of mono- and dichloro-1,2,5-thiadiazoles [20,21]. The next band at 13.8 eV is assigned to two MOs, one is the third nitrogen lone pair, n_{N} , and the second is the second chlorine lone pair MO. The next band at 15.6 eV is assigned again to two orbitals, to the lowest energy π orbital and n_{S} . This latter, according to calculations, is strongly mixed with the σ framework. The corresponding n_{S} band is observed in the 13–15 eV region of the photoelectron spectra of 1,2,5-thiadiazoles [20,21]. The last band in the spectrum at 16.8 eV is assigned to one MO. An unambiguous assignment is not possible due to the delocalization over the entire σ framework; calculations indicate that the corresponding MO has some C–Cl character (see Figure 5).

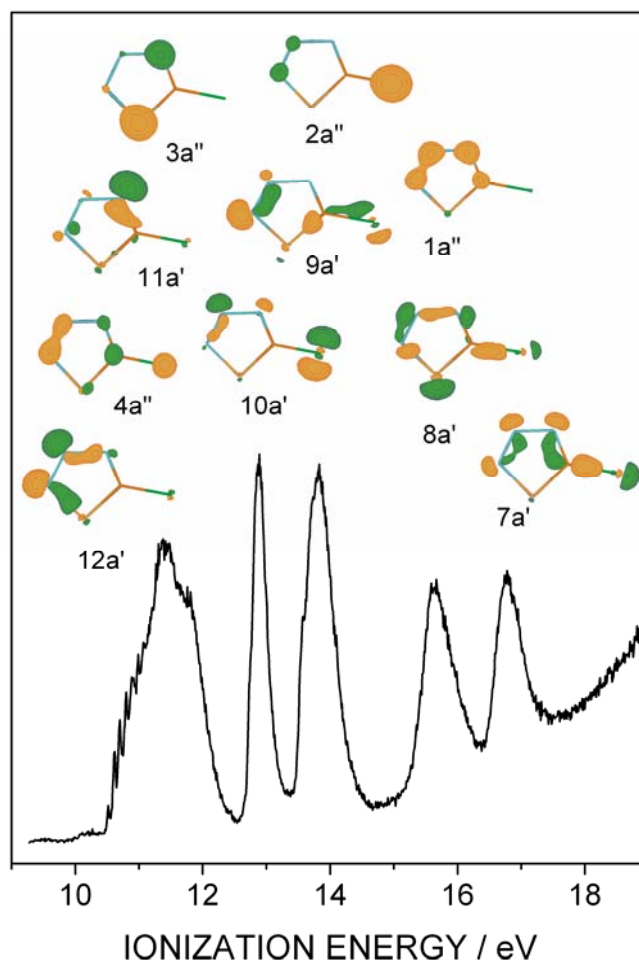


Fig. 5 He I photoelectron spectrum of 5-chloro-1,2,3,4-thiatriazole and schematics of the corresponding MOs

Table 5. Experimental and calculated^a vertical ionization energies (eV) of 5-chloro-1,2,3,4-thiatriazole

experimental	SAC-CI ^c	OVGF	orbital character
10.52 ^b	10.44 [0.95 (12a'), 0.11(10a')] 10.90 [−0.93 (4a''), −0.27(3a'')]	10.99 11.20	σ (n_N) π_3
11.4	11.08 [0.89 (11a'), −0.34 (10a')]	11.80	σ (n_N)
11.8	11.35 [0.93 (3a''), −0.28 (4a'')]	11.56	π_2
12.88	12.58 [0.83 (10a'), 0.36 (11a'), −0.28 (9a')]	12.91	σ (n_{Cl})
13.8	13.48 [0.88 (9a'), 0.32 (10a'), 0.17 (7a')] 13.86 [0.96 (2a'')]	14.05 13.90	σ (n_N) σ (n_{Cl})
15.6	15.61 [−0.91 (8a'), 0.21 (7a'), −0.15 (9a')] 16.09 [−0.93 (1a'')]	16.01 16.32	σ (n_S) π_1
16.8	16.74 [0.89 (7a'), 0.27 (8a'), −0.19 (9a')]	16.91	σ (C-Cl)

^a Calculated at the SAC-CI//CCSD(T)/aug-cc-pVTZ level. ^b Adiabatic ionization energy. Cationic vibrational wavenumber: 810±50 cm^{−1}. ^c Open-shell occupancy for single excitations and SAC-CI coefficients ($|c_i| > 0.1$) are provided in parenthesis.

Gas-phase thermolysis

The thermal decomposition of 5-chloro-1,2,3,4-thiatriazole is interesting not only from the viewpoint of high energy materials, but the generation of small reactive species, such as N_2S and chloro-pseudohalides. Thermolysis of the thiatriazole was carried out in the gas phase in an empty quartz tube. The effluent from the tube was continuously monitored by UPS and IR. Decomposition of thiatriazole commenced at 150 °C, and destruction was complete at 300 °C (see photoelectron spectra in Figure 6). Spectroscopies indicated the formation of ClCN and N_2 as major products, and the precipitation of elemental sulfur on the glassware was visually observed. Only two weak photoelectron bands at 10.53 and 11.42 eV indicate the formation of trace amounts of other side products. Side products have not been detected in IR. The photoelectron band at 10.53 eV is tentatively assigned to ClSCN on the basis of previously published photoelectron spectrum of ClSCN [22]. It is interesting to note that N_2S was not detected by UPS or IR spectroscopy in our experiments, neither S_2 , the primary product of bimolecular reactions of N_2S molecules. In contrast, N_2S and S_2 were observed by UPS as products of the gas-phase thermolysis of 5-phenyl-1,2,3,4-thiatriazole [15]. It was commented in this latter work that N_2S was very reactive and a bimolecular decomposition of N_2S was also occurring during thermolysis and effluent flow between the end of pyrolysis tube and intersecting ionizing beam (even at a short distance of about 1 cm) [15]. Although it is likely that N_2S forms during the thermolysis of 5-chloro-1,2,3,4-thiatriazole, we could not identify it. N_2S is a reactive intermediate and it possibly decomposes in the relatively long pyrolysis tube (30 cm) and during the relatively long effluent flow between furnace and detection point (40 cm).

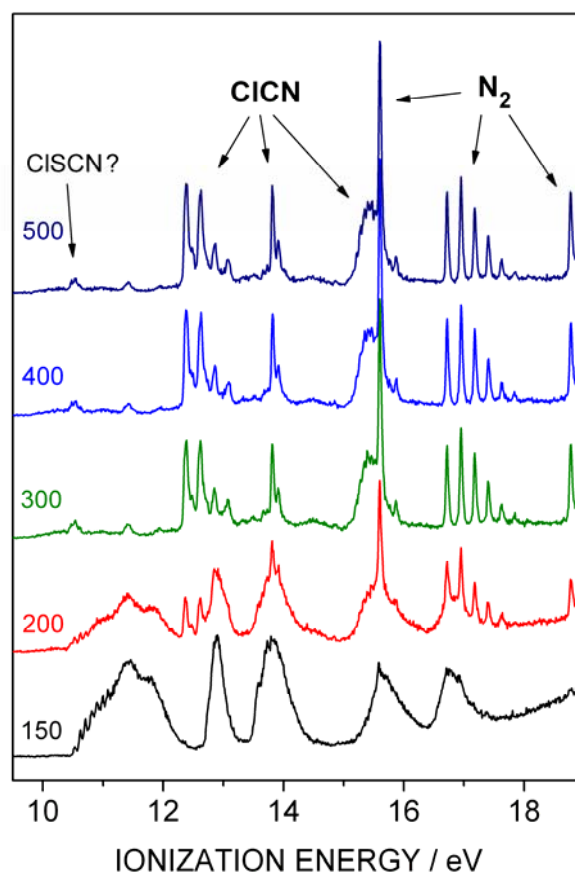


Fig. 6 Thermal decomposition of 5-chloro-1,2,3,4-thiatriazole (identified decomposition products and the temperature of the thermolysis, in °C, is shown).

Conclusions

The electronic, geometric, and vibrational properties, as well as thermal decomposition of 5-chloro-1,2,3,4-thiatriazole have been investigated in the gas phase by infrared spectroscopy, photoelectron spectroscopy, and theoretical calculations. According to calculations, the molecule has planar structure and C_s symmetry. It is predicted to decompose, via the formation of N_2S or chlorothiocarbonyl azide intermediates, to N_2 , $CICN$, and sulfur. The infrared and photoelectron spectroscopy has provided information on the fundamental vibrations and on the valence occupied levels of the neutral molecule, and on the sequence of the low-lying cationic states. 5-chloro-1,2,3,4-thiatriazole is thermally unstable, and gas-phase pyrolysis leads to N_2 , $CICN$, and sulfur.

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